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Crystal Engineering and Structural Investigations of the 2-Amino-5-nitropyridinium Salts $C_5H_6N_3O_2^+.HSO_4^-$ and $C_5H_6N_3O_2^+.H_2AsO_4^-$

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Abstract

The aim of studying the encapsulation of 2-amino-5-nitropyridinium cations in $(HSO_4^-)_n$ and $(H_2AsO_4^-)_n$ polymeric host matrices is to build acentric frameworks that are efficient for quadratic non-linear optical applications. Evidence is given for the role of inorganic polyanions in the formation of polar packings and this is discussed on the basis of X-ray crystal structure investigations. $C_5H_6N_3O_2^+.HSO_4^-$ is orthorhombic, *Pcab*, with $a = 29.617\,(9)$, $b = 13.185\,(3)$, $c = 9.013\,(2)$ Å, $Z = 16$: the crystal structure has been solved using direct methods and difference Fourier syntheses, with a reliability factor $R = 0.049$ for 2483 independent reflections. $C_5H_6N_3O_2^+.H_2AsO_4^-$ is orthorhombic, *Pna*2$_1$, $a = 25.777\,(5)$, $b = 6.333\,(2)$, $c = 5.814\,(4)$ Å, $Z = 4$: the crystal structure has been solved following the same route as employed for $C_5H_6N_3O_2^+.HSO_4^-$. The final R value is 0.040 for 1707 independent reflections.

Introduction

The chemical syntheses of the 2-amino-5-nitro-pyridinium monohydrogensulfate and dihydrogen-arsenate illustrate a new approach in the design of non-linear optical crystals where the inorganic host matrices can play a predominant role in the building of the acentric packing of non-linear optical organic cations. Such a crystal engineering route combines the cohesion and flexibility of anionic inorganic lattices with the enhanced polarizability of organic entities. The advantages of this crystal engineering strategy are: (1) the anchorage of organic cations onto inorganic subnetworks through multiple and short hydrogen bonds providing the packing with the cohesion observed in ionic inorganic crystals; (2) a blue shift of the crystal transparency resulting from the less polarizable nature of the protonated 2-amino-5-nitropyridinium cation as compared to an equivalent purely organic crystal (Dewar, 1950); (3) the building of acentric frameworks without using polarizable chiral entities: only the shielding effect from adequate inorganic polyanions favours the expected polar packing.

Among the nitroaniline derivatives, 2-amino-5-nitropyridine has been used as a model to be encapsulated in many anionic subnetworks (Table 1). Through several crystal structure determinations, we have observed that a shielding effect originating from anionic matrices is responsible for the acentric packing of 2-amino-5-nitropyridinium cations in such crystals. The crystal structures of these new 2-amino-5-nitropyridine salts were investigated with a view to identifying the precise location of non-linear optical cations with respect to the $(HSO_4^-)_n$ polymeric chain or $(H_2AsO_4^-)_n$ layered polyanion and hence providing evidence for a possible 'herringbone' arrangement of cations.

2-Amino-5-nitropyridinium monohydrogensulfate: $C_5H_6N_3O_2^+.HSO_4^-$ (2A5NPS)

Synthesis

2-Amino-5-nitropyridine (0.01 mol) was dissolved in 50 cm^3 of an acidic solution containing 0.0354 mol H_2SO_4 ($d = 1.835$), heated to 333 K. A crystalline precipitate was formed. After filtration and dissolution in an excess of H_2SO_4 the solution was slowly evaporated at room temperature. Prismatic orthorhombic crystals up to $0.60 \times 0.80 \times 0.90$ mm in size were yielded. The chemical formula was found on the basis of crystal-structure determination.

$$C_5H_5N_3O_2 + H_2SO_4 \rightarrow C_5H_6N_3O_2^+.HSO_4^-$$
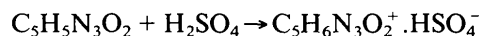
Structural investigation

For data collection, a prismatic single crystal, with dimensions $0.47 \times 0.70 \times 0.78$ mm, was selected.

Table 1. *Relationship between anionic steric hindrance and resulting polar packing*

	$(NO_3)^-$	$(CuCl_4)^{2-}$	$(COO^-)_2$	$(Cr_2O_7)^{2-}$	$(SO_4)^{2-}$	$(HSO_4^-)_n$	$(H_2PO_4^-)_n$	$(C_4H_5O_6^-)_n$
SHG powder test	−	−	−	+	−	−	+	+
Crystal symmetry	$P2_1/n$	$P2_1/c$		$P2_1nb$		$Pcab$	$Pna2_1$	$P2_1$
Solved structure	Yes	Yes	No	Yes	No	Yes	Yes	Yes
Situation of 2A5NP$^+$ cations	Antiparallel ordering	One site has polar ordering		Polar packing with pseudo-inversion centres		Antiparallel ordering	Polar packing	Polar packing
Average volume of anionic unit ($Å^3$)	50	147		150	80	80	85	140
References		Bagieu-Beucher et al. (1991)		Pecaut & Masse (1993)		This work	Masse & Zyss (1991)	Zyss, Masse, Bagieu-Beucher & Levy (1992)

Table 2. *Crystal data and experimental parameters for intensity data collection for 2A5NPS*

Cell parameters (Å)	$a = 29.617\,(9)$, $b = 13.185\,(13)$, $c = 9.013\,(2)$
$V\,(Å^3)$, M_r	3519 (3), 237.19
Z	16
D_x (Mg m^{-3})	1.791
Space group	$Pcab$
μ(Ag $K\alpha$) (cm^{-1})	2.084
Apparatus	Philips PW 1100 diffractometer
Wavelength (Å)	Ag $K\alpha = 0.5608$
Monochromator	Graphite plate
Scan mode	ω
θ range ($°$)	3–30
Scan width ($°$)	1.2
Scan speed ($° s^{-1}$)	0.02
Number of collected reflections	3072
hkl	$h_{max} = 37$, $k_{max} = 17$, $l_{max} = 11$
Total background measuring time (s)	10
Reference reflections	860 and 026

Experimental conditions and crystal data used during the measurement of diffracted intensities are given in Table 2. Orthorhombic unit-cell parameters were refined by a least-squares method using the angular data of 21 reflections ($8.5 < \theta < 11°$) measured with a four-circle diffractometer before data collection. Lorentz and polarization corrections were made. No absorption correction was applied. The structure was solved by direct methods (Main, Lessinger, Germain, Declercq & Woolfson, 1977) and H atoms were located by difference Fourier syntheses. Full-matrix least-squares refinements were performed on F, with the weighting scheme $w = 4F^2/\sigma(I)^2 + (pF^2)^2$, $p = 0.01$. After the final refinement cycles with anisotropic thermal parameters for all atoms except H atoms, the final R value was 0.049 for 2483 independent reflections [reflections with $I_o < 3\sigma(I_o)$ were rejected; $wR = 0.041$]. The maximum and minimum peak heights in the final difference Fourier map were $+0.40$ and -0.47 e Å^{-3}. All the calculations were carried out with the Enraf–Nonius *Structure Determination Package* (Enraf–Nonius, 1977) on a MicroVAX II computer. Scattering factors for neutral atoms and f', f'' were taken from *International Tables for X-ray Crystallography* (Cromer & Waber, 1977). The crystal structure representations were drawn using mainly *MOLDRAW* (Cense, 1989)

and *STRUPLO*84 (Fischer, 1985) programs. Table 3 displays the atomic coordinates.*

Description

The crystal structure of 2A5NPS (Fig. 1) displays alternating polar and antiparallel corrugated layers. Each layer contains $(HSO_4^-)_n$ polymeric files anchoring the 2-amino-5-nitropyridinium cations through short hydrogen bonds resulting in complete centrosymmetrical packing. The chains of sulfate anions are built up from HSO_4 units, the geometrical features of which are indicated in Table 4. Short hydrogen bonds [donor–acceptor = 2.573 (3) and 2.577 (3) Å] connect HSO_4 tetrahedral units to form infinite chains located at $\pm(a, b/4)$, $\pm(a/2, b/4)$, $\pm(a/4, b)$ and $\pm(a/4, b/2)$. Fig. 2 represents two chains lying in the *bc* plane. Three other parallel planes in the unit cell, at $a/2$ and $\pm a/4$, contain $(HSO_4^-)_n$ infinite chains. The distance between two adjacent sulfur atoms in a chain is S—S $\simeq 4.65$ Å and between two coplanar chains S—S $> b/2 = 6.6$ Å.
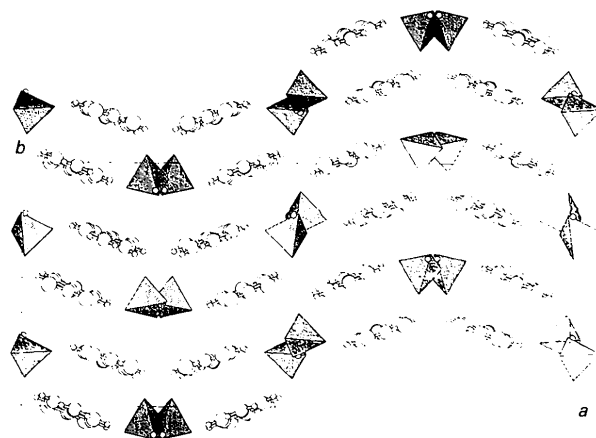
Fig. 1. Organic–inorganic corrugated layers in the 2-amino-5-nitropyridinium monohydrogensulfate structure.

Table 3. *Atomic coordinates, B_{eq} (Å^2) for non-H atoms and B_{iso} (Å^2) for H atoms with e.s.d.'s in parentheses*

$$B_{eq} = (4/3)\Sigma_i\Sigma_j\beta_{ij}\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	B_{eq}, B_{iso}*
S(1)	0.72995 (3)	0.06437 (7)	0.37618 (9)	2.47 (2)
O(11)	0.72500 (8)	−0.0360 (2)	0.3147 (2)	3.39 (6)
O(12)	0.68828 (7)	0.1053 (2)	0.4303 (3)	3.74 (6)
O(13)	0.76570 (7)	0.0689 (2)	0.4848 (3)	4.01 (6)
O(14)	0.7468 (1)	0.1349 (2)	0.2504 (3)	5.10 (6)
H(13)	0.742 (1)	0.114 (2)	0.169 (3)	5.2 (9)
S(2)	0.51131 (3)	−0.20777 (7)	−0.58281 (9)	2.72 (2)
O(21)	0.47992 (7)	−0.2160 (2)	−0.7062 (2)	3.79 (6)
O(22)	0.55676 (7)	−0.2283 (3)	−0.6236 (3)	5.92 (8)
O(23)	0.49573 (9)	−0.2946 (2)	−0.4803 (3)	4.46 (6)
O(24)	0.50597 (9)	−0.1147 (2)	−0.5029 (3)	4.84 (6)
H(14)	0.505 (1)	−0.290 (3)	−0.404 (3)	5.8 (9)*
C(11)	0.6600 (1)	−0.1922 (2)	−0.1414 (3)	2.43 (7)
C(12)	0.6160 (1)	−0.2228 (3)	0.0713 (4)	2.53 (7)
C(13)	0.6513 (1)	0.1880 (2)	0.1592 (3)	2.42 (7)
C(14)	0.6194 (1)	−0.2240 (3)	−0.0773 (4)	2.55 (7)
C(15)	0.6946 (1)	−0.1582 (3)	−0.0591 (4)	2.84 (7)
N(11)	0.6646 (1)	−0.1900 (2)	−0.3032 (3)	3.52 (7)
N(12)	0.64945 (9)	−0.1847 (2)	0.3049 (3)	3.56 (7)
N(13)	0.68926 (8)	−0.1551 (2)	0.0902 (3)	2.87 (6)
O(1)	0.63121 (9)	−0.2121 (2)	−0.3748 (2)	4.86 (7)
O(2)	0.70061 (9)	−0.1639 (2)	0.3569 (3)	4.98 (7)
H(1)	0.5951 (9)	−0.244 (2)	−0.135 (3)	3.3 (7)*
H(2)	0.5915 (8)	−0.238 (2)	0.107 (3)	2.1 (6)*
H(3)	0.6699 (9)	−0.161 (2)	0.344 (3)	2.5 (7)*
H(4)	0.7218 (8)	−0.138 (2)	−0.092 (3)	2.6 (7)*
H(5)	0.707 (1)	−0.126 (2)	0.139 (3)	4.1 (8)*
H(6)	0.624 (1)	−0.199 (2)	0.340 (3)	4.3 (8)*
C(21)	0.5969 (1)	0.0157 (2)	−0.3634 (3)	2.44 (7)
C(22)	0.6295 (1)	0.0575 (3)	−0.1285 (4)	2.67 (7)
C(23)	0.5894 (1)	0.0252 (2)	−0.0625 (3)	2.33 (7)
C(24)	0.5555 (1)	−0.0142 (3)	−0.1430 (4)	2.60 (7)
C(25)	0.6328 (1)	0.0519 (3)	−0.2786 (4)	2.59 (7)
N(21)	0.5980 (1)	0.0138 (2)	−0.5106 (3)	3.46 (7)
N(22)	0.55979 (8)	−0.0180 (2)	−0.2920 (3)	2.72 (6)
N(23)	0.58520 (9)	0.0282 (2)	0.0994 (3)	3.23 (7)
O(3)	0.54986 (8)	0.0007 (2)	0.1552 (3)	4.59 (7)
O(4)	0.61789 (9)	0.0586 (2)	0.1678 (3)	5.26 (7)
H(7)	0.656 (1)	0.083 (2)	−0.071 (4)	4.1 (8)*
H(8)	0.6575 (8)	0.073 (2)	0.316 (3)	1.7 (6)*
H(9)	0.539 (1)	−0.044 (2)	−0.338 (3)	4.5 (8)*
H(10)	0.5286 (8)	−0.036 (2)	−0.103 (3)	2.5 (7)*
H(11)	0.622 (1)	0.040 (2)	−0.551 (4)	5.4 (9)*
H(12)	0.547 (1)	−0.002 (2)	−0.549 (4)	4.3 (8)*

Symmetry code in *Pcab*: $x, y, z; -x, -y, -z; -x, \frac{1}{2}-y, \frac{1}{2}+z; x, \frac{1}{2}+y, \frac{1}{2}-z; \frac{1}{2}-x, \frac{1}{2}+y, -z; \frac{1}{2}+x, \frac{1}{2}-y, z; \frac{1}{2}+x, -y, \frac{1}{2}-z; \frac{1}{2}-x, y, \frac{1}{2}+z.$

Table 4. *Main interatomic distances (Å) and bond angles ($°$) for 2A5NPS with e.s.d.'s in parentheses*

First SO_4 tetrahedron in (HSO_4)$^-$ anion

S(1)	O(11)	O(12)	O(13)	O(14)
O(11)	1.443 (2)	2.396 (3)	2.391 (3)	2.415 (3)
O(12)	112.9 (1)	1.432 (2)	2.394 (3)	2.406 (3)
O(13)	111.9 (1)	112.7 (1)	1.444 (2)	2.353 (3)
O(14)	107.6 (1)	107.5 (2)	103.6 (2)	1.550 (3)

S(1)—O(14)—H(13)   114 (2)

Second SO_4 tetrahedron in (HSO_4)$^-$ anion

S(2)	O(21)	O(22)	O(23)	O(24)
O(21)	1.454 (2)	2.400 (3)	2.332 (3)	2.396 (3)
O(22)	113.2 (1)	1.422 (2)	2.388 (3)	2.385 (4)
O(23)	102.2 (1)	107.3 (2)	1.542 (3)	2.400 (3)
O(24)	112.3 (2)	113.4 (2)	107.6 (1)	1.432 (3)

S(2)—O(23)—H(14)   113 (3)

Table 4 (cont.)

First 2-amino-5-nitropyridinium cation site

C(11)—C(14)	1.398 (4)	C(14)—C(11)—C(15)	121.9 (3)
C(11)—C(15)	1.341 (5)	C(14)—C(11)—N(11)	119.8 (3)
C(11)—N(11)	1.465 (4)	C(15)—C(11)—N(11)	118.3 (3)
C(12)—C(13)	1.390 (4)	C(13)—C(12)—C(14)	121.0 (3)
C(12)—C(14)	1.344 (5)	C(13)—C(12)—H(2)	122 (2)
C(12)—H(2)	0.81 (2)	C(14)—C(12)—H(2)	117 (2)
C(13)—N(12)	1.316 (4)	C(12)—C(13)—N(12)	123.2 (3)
C(13)—N(13)	1.355 (4)	C(12)—C(13)—N(13)	118.0 (3)
C(14)—H(1)	0.92 (3)	N(12)—C(13)—N(13)	118.9 (3)
C(15)—N(13)	1.355 (4)	C(11)—C(14)—C(12)	118.3 (3)
C(15)—H(4)	0.90 (2)	C(11)—C(14)—H(1)	122 (2)
N(11)—O(1)	1.216 (4)	C(12)—C(14)—H(1)	120 (2)
N(11)—O(2)	1.222 (4)	C(11)—C(15)—N(13)	118.1 (3)
N(12)—H(3)	0.77 (3)	C(11)—C(15)—H(4)	129 (3)
N(12)—H(6)	0.85 (3)	N(13)—C(15)—H(4)	115 (2)
N(13)—H(5)	0.78 (3)	C(11)—N(11)—O(1)	116.7 (3)
		C(11)—N(11)—O(2)	118.7 (3)
		O(1)—N(11)—O(2)	124.6 (3)
		C(13)—N(12)—H(3)	116 (2)
		C(13)—N(12)—H(6)	114 (2)
		H(3)—N(12)—H(6)	129 (3)
		C(13)—N(13)—C(15)	122.8 (3)
		C(13)—N(13)—H(5)	116 (2)
		C(15)—N(13)—H(5)	120 (2)

Second 2-amino-5-nitropyridinium cation site

C(21)—C(25)	1.396 (4)	C(25)—C(21)—N(21)	122.3 (3)
C(21)—N(21)	1.327 (4)	C(25)—C(21)—N(22)	118.2 (3)
C(21)—N(22)	1.349 (4)	N(21)—C(21)—N(22)	119.5 (3)
C(22)—C(23)	1.396 (4)	C(23)—C(22)—C(25)	118.1 (3)
C(22)—C(25)	1.358 (4)	C(23)—C(22)—H(7)	123 (2)
C(22)—H(7)	1.00 (3)	C(25)—C(22)—H(7)	119 (2)
C(23)—C(24)	1.343 (4)	C(22)—C(23)—C(24)	121.6 (3)
C(23)—N(23)	1.465 (4)	C(22)—C(23)—N(23)	119.3 (3)
C(24)—N(22)	1.350 (4)	C(24)—C(23)—N(23)	119.0 (3)
C(24)—H(10)	0.92 (3)	C(23)—C(24)—N(22)	118.8 (3)
C(25)—H(8)	0.85 (2)	C(23)—C(24)—H(10)	124 (2)
N(21)—H(11)	0.88 (3)	N(22)—C(24)—H(10)	118 (2)
N(21)—H(12)	0.83 (3)	C(21)—C(25)—C(22)	120.6 (3)
N(22)—H(9)	0.82 (3)	C(21)—C(25)—H(8)	124 (2)
N(23)—O(3)	1.217 (4)	C(22)—C(25)—H(8)	116 (2)
N(23)—O(4)	1.217 (4)	C(21)—N(21)—H(11)	116 (2)
		C(21)—N(21)—H(12)	113 (2)
		H(11)—N(21)—H(12)	130 (3)
		C(21)—N(22)—C(24)	122.7 (3)
		C(21)—N(22)—H(9)	120 (2)
		C(24)—N(22)—H(9)	118 (2)
		C(23)—N(23)—O(3)	118.5 (3)
		C(23)—N(23)—O(4)	116.5 (3)
		O(3)—N(23)—O(4)	125.0 (3)

Hydrogen bonds

	O(N)—H	H···O	O(N)···O	O(N)—H···O
O(14)—H(13)···O(13)	0.80 (3)	1.77 (3)	2.573 (3)	177 (3)
O(23)—H(14)···O(21)	0.74 (3)	1.84 (3)	2.577 (3)	173 (4)
N(12)—H(3)···O(11)	0.77 (3)	2.33 (3)	2.976 (4)	142 (2)
N(12)—H(6)···O(22)	0.85 (3)	2.05 (3)	2.878 (4)	167 (3)
N(13)—H(5)···O(11)	0.78 (3)	2.05 (3)	2.771 (3)	154 (3)
N(21)—H(12)···O(24)	0.83 (3)	2.53 (3)	3.211 (4)	141 (3)
N(21)—H(11)···O(12)	0.88 (3)	2.14 (3)	2.980 (4)	159 (3)
N(22)—H(9)···O(24)	0.82 (3)	2.00 (3)	2.789 (4)	160 (3)

These distances agree with values currently observed in inorganic salts containing the same (HSO_4^-)$_n$ polyanion (4.77 and 6 Å, respectively, in $KHSO_4$) (Cotton, Frenz & Hunter, 1975).

(HSO_4^-)$_\infty$ chains are surrounded by 2A5NP$^+$ ($C_5H_6N_3O_2^+$) ions *via* hydrogen bonds to form corrugated double layers (Fig. 1) located at $+b/4$ and $-b/4$. These double layers, related by a symmetry centre, are about 3.40 Å thick and separated by

3.25 Å. Each 2A5NP$^+$ cation is anchored onto two sulfate ions belonging to two different chains through three hydrogen bonds (Figs. 3–5). Geometrical features of the 2A5NP$^+$ cations described in Table 4 are similar to those observed in various 2-amino-5-nitropyridine salts (Masse & Zyss, 1991; Pecaut & Masse, 1993; Bagieu-Beucher, Masse & Tranqui, 1991). The pyridine-ring atoms are almost coplanar but the exocyclic atoms of the nitro group are significantly displaced from the mean plane. Twist angles between nitro groups and pyridine rings are 5.4 and 2.4°, respectively. The shortest distance between non-H atoms of two cationic rings belonging to independent double layers is C(14)—C(25) = 3.252 Å.

Compared to p-nitroaniline (pNA; Colapietro, Domenicano, Marciante & Portalone, 1982), the protonation of pyridine shortens all the conjugated bond lengths C—C, C—N and C—NH$_2$ [1.327 (4) and 1.316 (4) *versus* 1.355 (2) Å in pNA] in contrast to C—NO$_2$ distances [1.465 (4) and 1.465 (4) *versus* 1.434 (2) Å in pNA] which are slightly lengthened. Such bond-distance changes indicate an alteration in the intramolecular charge transfer, NH being an electron-acceptor group in competition with the electron-withdrawing NO$_2$ group. The presence of
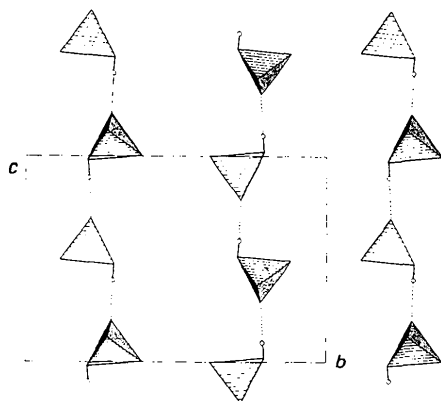
the protonated N heteroatom in the aromatic ring is believed to account for the inclination of the molecular transition dipole moment with respect to the nitro–amino direction in the non-protonated molecule. This protonation modifies the transparency of the original molecule (yellow) and consequently shifts the crystal transparency limit towards blue wavelengths, as observed in 2-amino-5-nitropyridinium dihydrogenmonophosphate (Kotler, Hierle, Josse, Zyss & Masse, 1992). The 2A5NPS crystals are colourless. The (HSO$_4^-$)$_n$ polymeric chains cannot efficiently screen the dipolar interactions of cationic entities resulting in a complete centrosymmetrical arrangement of framework; however, the nearly perfect orientation of organic cations following the **c** crystallographic direction observed in some layers (Fig. 3) suggests an increase in the thickness of the anionic wall favouring a non-centrosymmetrical packing. This strategy has been applied with the following crystal, using an (H$_2$AsO$_4^-$)$_n$ polymeric host matrix.
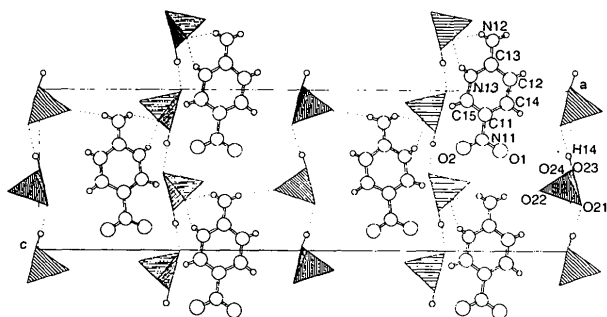

Fig. 2. (HSO$_4^-$)$_n$ chains lying in the **bc** plane.

Fig. 3. Layer running at $b = 1/4$ showing a quasi-perfect polar alignment of 2-amino-5-nitropyridinium cations.
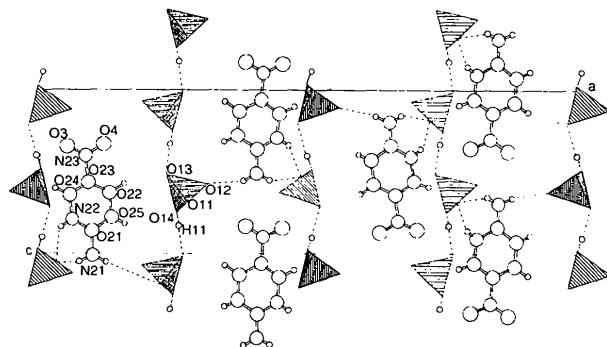

Fig. 4. Layer displaying an antiparallel arrangement of 2-amino-5-nitropyridinium cations.
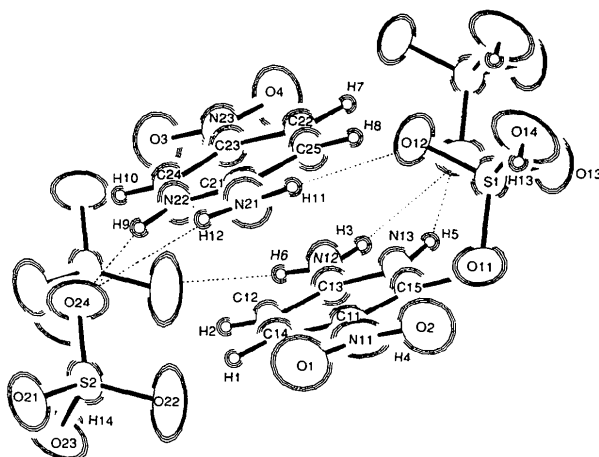

Fig. 5. Detailed connection of the 2-amino-5-nitropyridinium cations with the polymeric sulfate chains through *ORTEP* (Johnson, 1965) representation.

2-Amino-5-nitropyridinium dihydrogenmonoarsenate: $C_5H_6N_3O_2^+ \cdot H_2AsO_4^-$ (2A5NPDAs)

Synthesis

0.01 mol of 2-amino-5-nitropyridine was dissolved in 30 cm^3 of arsenic acid (1 mol dm^{-3}) at 333 K. After cooling to room temperature, the solution was filtered to eliminate excess 2-amino-5-nitropyridine. A slow evaporation yielded parallelepiped crystals up to 10 × 2 × 1 mm in size. The crystals were dried on filter paper to absorb residual mother acid solution. The chemical formula was determined on the basis of X-ray crystal structure investigation.

$$C_5H_5N_3O_2 + H_3AsO_4 \rightarrow C_5H_6N_3O_2^+ \cdot H_2AsO_4^-$$
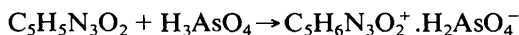
Structural investigation

Crystal data and experimental conditions used during the measurement of diffracted intensities are given in Table 5. The investigation was carried out as for 2A5NPS. For data collection, a parallelepiped single crystal (0.24 × 0.42 × 0.80 mm) was selected. Orthorhombic unit-cell parameters were refined by a least-squares method from the angular setting of 24 reflections ($10 < \theta < 12°$) measured with a four-circle diffractometer. A secondary-extinction coefficient was not refined. Full-matrix least-squares refinements were performed on F, using the weighting scheme $w = 4F^2/\sigma(I)^2 + (pF^2)^2$, $p = 0.01$. After the final refinement cycles with 1707 independent reflections, the final R value was 0.041, $wR = 0.040$. $I_o < 3\sigma(I_o)$ were rejected. Maximum shift/e.s.d. = 0.23. Maximum and minimum peak heights in the final difference Fourier map were +2.6 and -1.2 e Å^{-3} because of arsenic residual electron density. The third peak heights of the maps are less than 0.6 e Å^{-3} and more than -0.8 e Å^{-3}. Atomic coordinates are given in Table 6.*

Description

2A5NPDAs is isostructural with 2-amino-5-nitropyridinium dihydrogenmonophosphate (2A5NP-DP) (Masse & Zyss, 1991). $(H_2AsO_4^-)_n$ layers sandwich the 2-amino-5-nitropyridinium cations $(2A5NP^+)$ ordered in a herringbone network (Figs. 6 and 7). The anionic subnetwork is cohesive through short hydrogen bonds [donor–acceptor distance = 2.549 (5) and 2.767 (5) Å] (Fig. 8). Such an anionic wall screens the dipole–dipole interactions between the 2A5NP$^+$ cations better than $(HSO_4^-)_n$ chains in 2A5NPS, resulting in an acentric packing of the whole framework. The anchorage of cations onto the anionic layer through three hydrogen bonds (Table 7) makes the packing highly cohesive. From the point of view of polar crystal engineering the main

* See deposition footnote.

Table 5. Crystal data and experimental parameters for intensity data collection for 2A5NPDAs

Cell parameters (Å)	$a = 25.777$ (5), $b = 6.333$ (2), $c = 5.814$ (4)
V (Å^3), M_r	949.2 (8), 280.9
Z	4
D_x (Mg m^{-3})	1.966
Space group	$Pna2_1$
μ(Ag $K\alpha$) (cm^{-1})	20.14
Apparatus	Enraf–Nonius CAD-4 diffractometer
Wavelength (Å)	Ag $K\alpha = 0.5608$
Monochromator	Graphite plate
Scan mode	ω
θ range (°)	2–30
Scan width (°)	1.2
Scan speed (° s^{-1})	0.033–0.11
Higher measuring time of a reflection (s)	36.4
hkl	$h_{max} = 46$, $k_{max} = 11$, $l_{max} = 10$
Number of collected reflections	3347
Total background measuring time (s)	3.6–12.1
Reference reflections	$4\bar{1}4$ and 444

Table 6. Atomic coordinates, B_{eq} (Å^2) for non-H atoms and B_{iso} (Å^2) for H atoms with e.s.d.'s in parentheses

$$B_{eq} = (4/3)\Sigma_i\Sigma_j\beta_{ij}\mathbf{a}_i \cdot \mathbf{a}_j.$$

	x	y	z	B_{eq}, B_{iso}*
As	0.21167 (1)	0.13959 (6)	0.250	1.985 (5)
O(1)	0.2234 (1)	-0.1174 (4)	0.2719 (7)	2.65 (5)
O(2)	0.1937 (1)	0.2380 (7)	0.5137 (7)	3.41 (7)
O(3)	0.2676 (1)	0.2708 (8)	0.1911 (6)	4.79 (8)
O(4)	0.1641 (1)	0.1910 (5)	0.0689 (6)	2.79 (6)
C(1)	0.3816 (2)	0.1941 (7)	0.3737 (9)	2.35 (8)
C(2)	0.4141 (2)	0.0554 (6)	0.246 (2)	3.20 (8)
C(3)	0.4393 (2)	0.1246 (8)	0.0581 (1)	3.6 (1)
C(4)	0.4336 (2)	0.3340 (7)	0.9883 (9)	2.75 (9)
C(5)	0.4031 (2)	0.4690 (7)	0.1175 (9)	2.52 (8)
N(1)	0.3557 (2)	0.1313 (6)	0.5591 (9)	3.00 (8)
N(2)	0.4590 (2)	0.4146 (7)	0.7849 (9)	3.69 (9)
N(3)	0.3788 (1)	0.3974 (5)	0.3040 (6)	2.21 (7)
O(1N2)	0.4520 (1)	0.5987 (6)	0.7262 (8)	4.32 (8)
O(2N2)	0.4868 (2)	0.2907 (8)	0.6771 (8)	5.6 (1)
H(O2)	0.218 (2)	0.28 (1)	0.60 (1)	3 (1)*
H(O3)	0.271 (3)	0.32 (1)	0.05 (2)	5 (2)*
H(1N1)	0.348 (2)	-0.011 (7)	0.59 (1)	2 (1)*
H(2N1)	0.332 (2)	0.209 (8)	0.62 (1)	1 (1)*
H(N3)	0.362 (2)	0.492 (9)	0.35 (1)	3 (2)*
H(C2)	0.415 (2)	0.920 (7)	0.30 (1)	1(1)*
H(C3)	0.462 (2)	0.036 (8)	0.96 (1)	2 (1)*
H(C5)	0.403 (2)	0.625 (8)	0.08 (1)	3 (2)*

structural feature of 2A5NPDAs is the cation ordering in the herringbone structure. Similar arrangements have been observed in two other molecular analogues: 2-cyclooctylamino-5-nitropyridine (COANP, $Pca2_1$) (Gunter, Bosshard, Sutter, Arend, Chapuis, Twieg & Dobrowski, 1987) and 2-adamantylamino-5-nitropyridine (AANP, $Pna2_1$) (Nicoud, 1988; Tomaru, Matsumoto, Kurihasa, Suzuki, Ooba & Kaino, 1991). A detailed inspection of COANP, AANP and 2A5NPDAs crystal structures, where similarities are already suggested by comparable cell parameters and equivalent space groups, indicates that the $(H_2AsO_4^-)_n$ polyanion plays the same pivotal role as the cyclooctyl and adamantyl bulky groups in the formation of polar

Table 7. *Main interatomic distances* (Å) *and bond angles* (°) *for* 2A5NPDAs *with e.s.d.'s in parentheses*

AsO₄ tetrahedron in (H₂AsO₄)⁻ anion

As	O(1)	O(2)	O(3)	O(4)
O(1)	1.661 (3)	2.762 (5)	2.750 (5)	2.748 (4)
O(2)	109.6 (2)	1.719 (4)	2.681 (5)	2.713 (5)
O(3)	109.9 (2)	103.4 (2)	1.698 (4)	2.807 (5)
O(4)	112.2 (2)	107.3 (2)	114.0 (2)	1.649 (3)

As—O(3)—H(O3) 115 (5)   As—O(2)—H(O2)   116 (4)

2-Amino-5-nitropyridinium cation site

C(1)—C(2)	1.423 (8)	N(3)—C(1)—C(2)	117.5 (5)
C(1)—N(3)	1.352 (6)	N(3)—C(1)—N(1)	120.1 (4)
C(1)—N(1)	1.329 (7)	C(2)—C(1)—N(1)	122.3 (5)
C(2)—C(3)	1.34 (1)	C(1)—C(2)—C(3)	120.5 (5)
C(2)—H(C2)	0.91 (4)	C(1)—C(2)—H(C2)	115 (3)
C(3)—C(4)	1.395 (7)	C(3)—C(2)—H(C2)	125 (3)
C(3)—H(C3)	0.98 (6)	C(2)—C(3)—C(4)	119.7 (5)
C(4)—C(5)	1.383 (7)	C(2)—C(3)—H(C3)	124 (4)
C(4)—N(2)	1.445 (7)	C(4)—C(3)—H(C3)	117 (4)
C(5)—N(3)	1.333 (6)	C(3)—C(4)—C(5)	119.3 (5)
C(5)—H(C5)	1.01 (5)	C(3)—C(4)—N(2)	121.8 (5)
N(3)—H(N3)	0.79 (6)	C(5)—C(4)—N(2)	118.9 (4)
N(1)—H(1N1)	0.94 (5)	C(4)—C(5)—N(3)	119.9 (4)
N(1)—H(2N1)	0.87 (5)	C(4)—C(5)—H(C5)	119 (4)
N(2)—O(1N2)	1.228 (6)	N(3)—C(5)—H(C5)	121 (4)
N(2)—O(2N2)	1.235 (7)	C(5)—N(3)—C(1)	122.9 (4)
		C(5)—N(3)—H(N3)	108 (5)
		C(1)—N(3)—H(N3)	129 (5)
		C(1)—N(1)—H(1N1)	123 (4)
		C(1)—N(1)—H(2N1)	121 (4)
		H(1N1)—N(1)—H(2N1)	109 (5)
		C(4)—N(2)—O(1N2)	119.8 (4)
		C(4)—N(2)—O(2N2)	117.0 (4)
		O(1N2)—N(2)—O(2N2)	123.2 (5)

Hydrogen bonds

	O(N)—H	H···O	O(N)···O	O(N)—H···O
O(2)—H(O2)···O(1)	0.85 (6)	1.92 (6)	2.768 (5)	175 (6)
O(3)—H(O3)···O(1)	0.85 (10)	1.7 (1)	2.549 (5)	174 (7)
N(1)—H(2N1)···O(1)	0.86 (5)	2.01 (5)	2.867 (5)	178 (4)
N(3)—H(N3)···O(4)	0.78 (6)	1.91 (7)	2.655 (5)	158 (7)
N(1)—H(1N1)···O(4)	0.94 (5)	1.92 (5)	2.835 (5)	165 (7)

structure. A second harmonic generation powder test (Kurtz & Perry, 1968) performed on 2A5NPDAs with a YAG:Nd³⁺ fundamental beam (1.06 μm) illumination is comparable to that of 2A5NPDP: the quadratic non-linear optical properties of 2A5NPDP
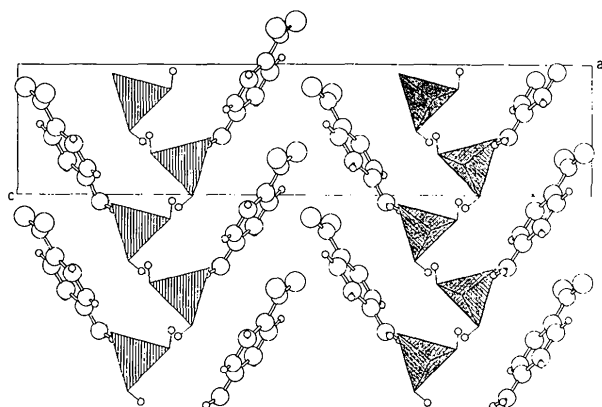
Fig. 6. Herringbone structure of 2-amino-5-nitropyridinium dihydrogenarsenate viewed along the *b* axis.

have been recently reported (Kotler *et al.*, 1992) with favourable phase-matching conditions for second harmonic generation in the $\lambda = 1$ μm region. The non-linear optical properties of 2A5NPDAs will be further studied. The same remarks as developed for 2A5NPS can be applied to the geometry of the 2A5NP⁺ cation (Table 7): the shortening of all the conjugated bonds in the cation with respect to the original bonds in the molecule is connected to the increase of transparency range towards the visible and UV region.

Concluding remarks

The crystal structure of 2A5NPS displays layers in which the 2-amino-5-nitropyridinium cations are quasi-perfectly orientated along the [001] direction: such a situation could favour the electrooptic coefficient along this direction if all the framework were to be acentric! Evidence for an identical and perfect cationic arrangement has been given in the polar structure of the 2-amino-5-nitropyridinium L-monohydrogentartrate salt (Zyss, Masse, Bagieu-Beucher & Levy, 1992), emphasizing the role of the polymeric anion chain (dimension and charge) in efficiently screening the dipolar interactions between cations. 2A5NPDAs isostructural with 2A5NPDP also displays the shielding effect of an (H₂AsO₄⁻)ₙ
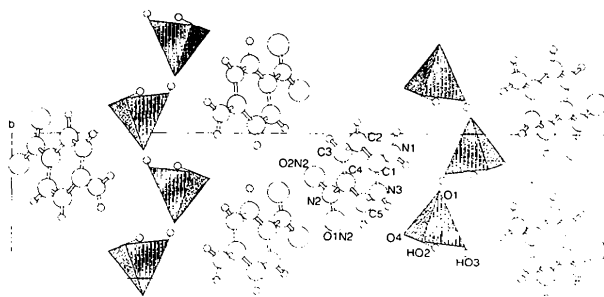
Fig. 7. Detailed hydrogen-bond scheme in 2-amino-5-nitropyridinium dihydrogenarsenate showing the connection between organic and inorganic networks.
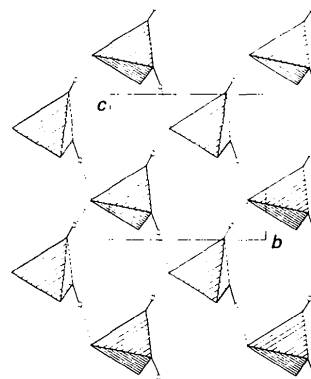
Fig. 8. **bc** projection of the (H₂AsO₄⁻)ₙ layered polyanion.

anionic layer in the formation of a herringbone cationic structure. In the design of crystals containing 2-amino-5-nitropyridinium polar arrangements, the parameters which govern the non-centrosymmetry are the dimensions and charge of associated counter-anions (Table 1) which are able to dilute the organic cations in the expected structure: large individual anions or chained or layered polymeric aggregates can be useful tools to induce acentric crystalline frameworks. Advantages of such organic salts compared to molecular salts include relatively easy crystal growth and crystal transparency.

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Crystal Structures and Polymorphism in Aliphatic *p*-Amidobenzoic Acids

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Abstract

(I) *p*-Propanamidobenzoic acid acetic acid solvate, $C_{10}H_{11}NO_3.\frac{1}{2}C_2H_4O_2$, $M_r = 223.23$, monoclinic, $P2_1/n$, $a = 5.135$ (1), $b = 24.556$ (5), $c = 9.496$ (2) Å, $\beta = 105.33$ (3)°, $V = 1155$ Å^3, $Z = 4$, $D_x = 1.28$ g cm^{-3}, λ(Mo $K\alpha$) $= 0.71069$ Å, $\mu = 0.095$ mm^{-1}, $F(000) = 472$, $T = 295$ K, $R = 0.062$ for 1108 observed reflections. (II) *p*-Butanamidobenzoic acid, $C_{11}H_{13}NO_3$, $M_r = 207.23$, triclinic, $P\bar{1}$, $a = 5.120$ (6), $b = 6.595$ (2), $c = 15.786$ (3) Å, $\alpha = 100.98$ (2), $\beta = 94.48$ (5), $\gamma = 98.15$ (5)°, $V = 515$ Å^3, $Z = 2$, $D_x = 1.34$ g cm^{-3}, λ(Mo $K\alpha$) $= 0.71069$ Å, $\mu = 0.091$ mm^{-1}, $F(000) = 220$, $T = 295$ K, $R = 0.078$ for 1229 observed reflections. (III) *p*-

Pentanamidobenzoic acid, $C_{12}H_{15}NO_3$, $M_r = 221.26$, monoclinic, $P2_1/c$, $a = 5.081$ (4), $b = 24.066$ (6), $c = 9.662$ (4) Å, $\beta = 82.06$ (6)°, $V = 1170$ Å^3, $Z = 4$, $D_x = 1.26$ g cm^{-3}, λ(Mo $K\alpha$) $= 0.71069$ Å, $\mu = 0.084$ mm^{-1}, $F(000) = 472$, $T = 295$ K, $R = 0.057$ for 1673 observed reflections. (IV) *p*-Nonanamidobenzoic acid, $C_{16}H_{23}NO_3$, $M_r = 277.36$, triclinic, $P\bar{1}$, $a = 5.176$ (1), $b = 6.731$ (5), $c = 22.127$ (17) Å, $\alpha = 92.79$ (6), $\beta = 91.13$ (4), $\gamma = 100.04$ (4)°, $V = 758$ Å^3, $Z = 2$, $D_x = 1.22$ g cm^{-3}, λ(Mo $K\alpha$) $= 0.71069$ Å, $\mu = 0.078$ mm^{-1}, $F(000) = 300$, $T = 295$ K, $R = 0.119$ for 1178 observed reflections. The effect of varying alkyl chain length upon the hydrogen-bonding pattern for a series of aliphatic amidobenzoic acids has been investigated. (II) and (IV) are isostructural. Acid dimers are formed, with the dimers further

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